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Research Article

ONE-POT SYNTHESIS OF THE COUMARINE UNDER GREEN APPROACH USING FERROUS SULPHATE AS CATALYST

Gurumeet C. Wadhawa [1]*, Harshada Deshmukh [2], Vitthal S. Shivankar [3], Yashwant A. Gaikwad [4]

*[1] Assistant Professor at Post Graduate Department of Chemistry, Karmaveer Bhaurao Patil College, Vashi sector 15 A, Navi Mumbai, 400703, Maharashtra, INDIA.

[2] Student, Post Graduate Department of Chemistry, Karmaveer Bhaurao Patil College, Vashi sector 15 A, Navi Mumbai, 400703, Maharashtra, INDIA.

[3] Principal, Post Graduate Department of Chemistry, Karmaveer Bhaurao Patil College, Vashi sector 15 A, Navi Mumbai, 400703, Maharashtra, INDIA.

[4] Assistant Professor, Post Graduate Department of Chemistry, Karmaveer Bhaurao Patil College, Vashi sector 15 A, Navi Mumbai, 400703, Maharashtra, INDIA.

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ABSTRACT

Synthesis of various substituted Coumarins from substituted phenol and β-ketoester (Ethyl Acetoacetate) via Pechmann condensation using heterogeneous catalyst like red mud solvent free condition under sonication. Reaction required low reaction time, very mild reaction condition, at room temperature and easy workup with good yield of the product.

KEYWORDS: *Coumarins, Pechmann condensation, Solvent free reaction, Sonication.*

INTRODUCTION

The development of different heterogeneous catalysts for various fine chemical syntheses has become a major area of research.

The main advantages of these materials over homogeneous system are heterogeneous simplified recovery and reusability, the potential for incorporation in continuous reactors and micro reactors. Novel environmentally benign chemical procedures for use academia and industry for green approach [1].

Application of solid acids in organic transformations has on important role, because they have many advantages such as facile handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal [2-6]. Coumarine derivatives are natural products widely distributed in the plant kingdom and their main applications are as fragrance, pharmaceuticals, and agrochemicals other industries [7].

***Corresponding author:**
Gurumeet C. Wadhawa
Assistant Professor,
At Post Graduate Department of Chemistry,
Karmaveer Bhaurao Patil College,
Vashi sector 15 A, Navi Mumbai, 400703, Maharashtra, INDIA.
** E-Mail: gwadhava25@gmail.com*

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Coumarins and there derivatives plays very important role in area like medicinal chemistry, due to its very vast sector of biological activities [8] anti-cancer [9], Antibacterial [10], anti-inflammatory [11], anti-fungal [12], anti-pyretic, anti-biotic [13], and also reported for exhibiting photochemical properties [14]. Coumarins can be synthesized by various methods such as Pechmann [15], Perkins [16], Knoevengeal [17], Wittig Reaction [18] and Reformat sky [19] other chemical reactions. Pechmann condensation is most widely used one of the most common reactions for the synthesis of coumarins and derivatives. These reactions involves condensation of Phenols with β-ketoester in presences of various catalysts like H_2SO_4, $AlCl_3$, PPA, $FeCl_3$, $ZnCl_2$, $POCl_3$, TFAA, P_2O_5, various lewis acid catalyst. In recent years heterogeneous catalyst [20-25] are offering high possibilities in the synthetic methods.

In this current approach we are trying to easy workup, to reducing reaction time, very mild reaction condition, reusability of catalyst and specially enhancing product yield with purity. In this study we prepared a heterogeneous catalyst which is useful by means of very easy handling and after work done easy expelling from reaction for greener approach.

MATERIALS AND METHODS

General:

All the compounds used in synthesis were of synthetic grade, from S.D. Fine the melting points of the compounds were determined in open head capillary in paraffin and are uncorrected. The IR spectra of the compounds were recorded in the region of 4000- 400 cm-1 by on FT-IR scimanzdu spectrophotometer. H^1 NMR spectra were recorded on a DRX-300 Bruker FT-NMR spectrophotometer in $CDCl_3$. The values of

chemical shift are expressed in δ ppm as a unit. All the compounds were checked for purity by thin layer chromatography (TLC).

General procedure for the synthesis of Coumarins:

Substituted Phenols (10 mmol) and β- ketoester (EAA) (10 mmol), were taken with 10 mol % of red mud catalyst grind for few minutes, in mortar and pestle at room temperature, then subjected to sonication, completion of reaction checked using thin layer chromatography was added to reaction mixture and filtered to remove solid catalyst. Organic layer was wash with water (50 ml × 2) and evaporated in reduced pressure to obtained solid products finally recrystallized from suitable solvent.

Reaction Scheme:

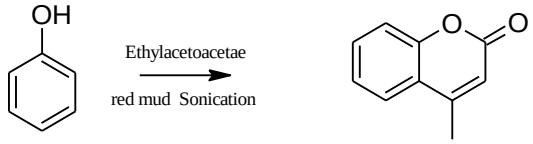
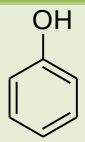
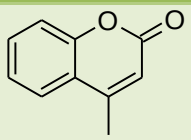
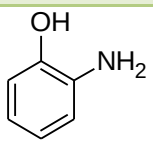
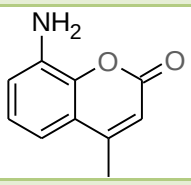
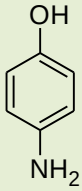
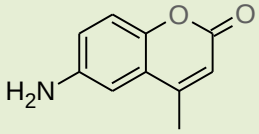
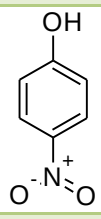
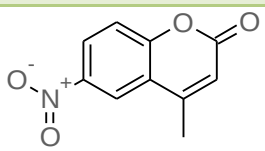
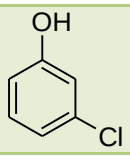
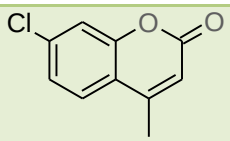
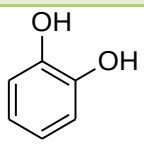
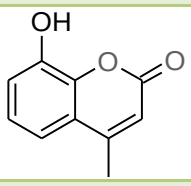
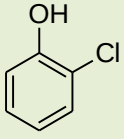
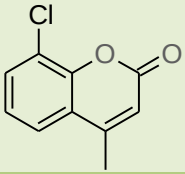
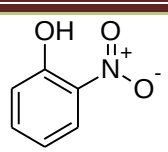
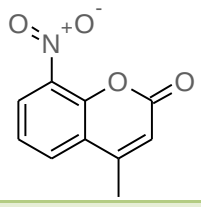
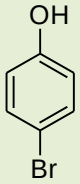
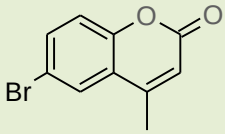
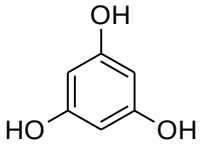
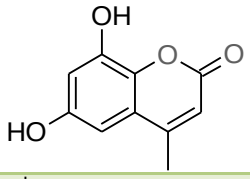
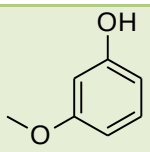
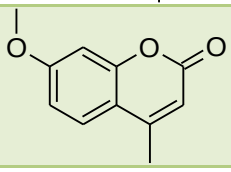
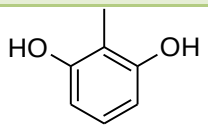
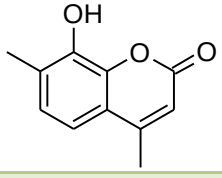
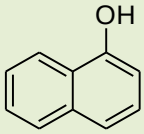
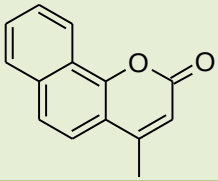
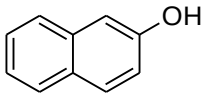
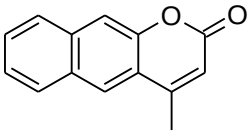


Table No. 1: Observation table for Coumarine Derivatives

Sr. No.	Phenol used	Product	Time in Min.	Melting point in ^{0}C
1			70	79
2			80	146
3			90	158
4			90	156
5			90	182
6			100	192
7			90	158

8			90	162
9			90	198
10			70	280
11			90	158
12			90	140
13			90	151
14			90	180

Spectral data:

1) 7-Hydroxy-4-methyl coumarin 1 H NMR (300 MHz, DMSO): δ 2.12 (3H, s, CH3), 6.18 (1H, s, CH), 6.16 (1H, s, ArH), 6.56 (1H, d, J = 8.5 Hz, ArH), 7.54 (1H, d, J = 8.75 Hz, ArH), 10.42 (1H, s, OH) ppm.
   IR (KBr): υ 3129, 1679, 1596, 1390 cm–1.
2) yellowish. 1H NMR (CDCl3) δ: 2.1 (s, 3H, Me), 5.9 (s, 1H), 6.8 (d, 1H, J 2.4 Hz), 6.97 (dd, 1H, J 8.7 and 2.4 Hz), 7.5 (d, 1H, J 8.7 Hz). IR (KBr, ν/cm -1): 2985, 1740, 1625.

RESULT AND DISCUSSION

We herein disclose a very simple and convenient method for the efficient synthesis of coumarins and their derivatives under sonication using red mud as catalyst.The experiment was conducted with phenolic substrate and β – keto –ester 2in the presence of catalytic amount red mud (20 mol%) in sonication . the reaction proceeded spontaneously at ambient temperature and was completed within 60-90 min. The isolated of product was straight forward as the solid precipitated on completion of the reaction. The precipitated on completion of the reaction. The precipitated solid was filtered, dried and washed with 20 % ethyl acetate in petroleum ether to offered coumar. The result provided the incentive for further study of reactions with various other phenolic, substrate and corresponding coumarins

CONCLUSION

We have developed simple, cost effective, product with high yield and purity with good % of purity, we have used greener approach for the synthesis.

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Conflict of interest: The authors have declared that no conflict of interest exists.

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